Acta Cryst. (1998). C**54**, 535–539

Phenolphthalein and 3′,3″-Dinitrophenolphthalein

Lawrence J. Fitzgerald and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

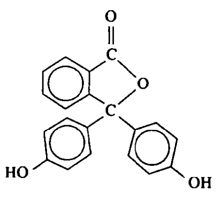
(*Received 22 July 1997; accepted 7 November 1997*)

Abstract

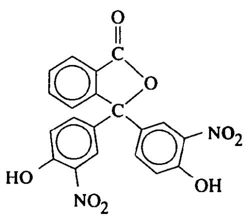
Phenolphthalein, $C_{20}H_{14}O_4$, crystallized in the non-centrosymmetric space group $Pna2_1$ with two crystallographically inequivalent molecules. Each of these is linked to four others of its own type by four hydrogen bonds having $O_{donor}\cdots O_{acceptor}$ distances ranging from 2.631 (4) to 2.787 (4) Å. While chains of hydrogen bonds propagate in a number of directions in this structure, cyclic hydrogen bonding is not observed. 3′,3″-Dinitrophenolphthalein, $C_{20}H_{12}N_2O_8$, crystallized in the centrosymmetric space group *Pbcn* with a single molecule in the asymmetric unit. Each molecule is linked to three others by four hydrogen bonds having $O_{donor}\cdots O_{acceptor}$ distances ranging from 2.572 (4) to 3.274 (3) Å. Although chains of hydrogen bonds are prominent in this structure, cyclic hydrogen bonding also occurs and forms dimers. As expected on the basis of the excess of potential acceptor O atoms over donors in both structures, significant C—H···O interactions are also abundant.

Comment

This is one of a series of studies of hydrogen bonding in organic solids, in this instance, in the structures of two diphenols: phenolphthalein, (I), and 3′,3″-dinitrophenolphthalein, (II). Each of these molecules also possesses a phthalide group which contains two O atoms which are potential hydrogen-bond acceptors, while (II) also contains a further four potential O-atom acceptors in its nitro groups.



(I)



(II)

In the structure of (I) there are two crystallographically inequivalent molecules, designated *A* and *B* and shown in Figs. 1(*a*) and 1(*b*), respectively, each of which is linked to four molecules of its own type by four hydrogen bonds. In these bonds, $O_{donor}\cdots O_{acceptor}$ distances range from 2.631 (4) to 2.787 (4) Å and O—H···O angles range from 162 (4) to 176 (5)°. Further geometric details are given in Table 2. These hydrogen bonds involve all the O atoms except the phthalide ring O atoms, O1*A* and O1*B*. For the purposes of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) these bonds are designated *A*(*a*), *A*(*b*), *B*(*a*) and *B*(*b*) in the order as given in Table 2. The first-level graph-set descriptors are then as follows: for *A*(*a*), *C*(10) propagating along [011]; for *A*(*b*), *C*(12) propagating along [001]; for *B*(*a*), *C*(10) propagating along [011]; for *B*(*b*), *C*(12) propagating along $[01\bar{1}]$. The basic second-level descriptors are: for *A*, $C_2^2(12)$ propagating along $[01\bar{2}]$, and for *B*, $C_2^2(12)$ propagating along [001]. Thus, through basic second-level graphs, only chains of hydrogen bonds are present in the structure. Since the *A* and *B* molecules are not hydrogen bonded to each other, further complexity is absent. As expected on the basis of the excess of potential hydrogen-bond acceptors over potential hydrogen-bond donors, there are numerous significant C—H···O attractive interactions. Those C—H···O sets for which either the C···O or H···O distance is less than the sum of the corresponding Bondi (1964) van der Waals radii and for which the C—H···O angle is greater than 90° are listed in Table 2. While four of these interactions involve only *A* or only *B* molecules, one crosslinks an *A* and a *B* molecule.

In the structure of (II), the asymmetric unit is a single molecule (Fig. 1*c*) which is linked to three others by four hydrogen bonds. In these bonds, $O_{donor}\cdots O_{acceptor}$ distances range from 2.572 (4) to 3.274 (3) Å and O—H···O angles range from 107 (3) to 146 (4)°. For graph-set analysis these bonds are designated (*a*)–(*d*) in order as given in Table 4; results of the analysis are presented in Table 5. The diversity of the descriptors [relative to (I)] is rather striking, but consistent with the presence of four additional potential O-atom acceptors in the nitro groups. Noteworthy are the formation of dimers by hydrogen bonds involving O4#, H4# and O2 in rings containing 20 atoms disposed about centers of symmetry, and the occurrence of a substantial number of chains of hydrogen bonds. Atoms O2, O3*B*#, O3*B**, O4# and O4* participate in these hydrogen bonds, while O3*A*#, O3*A** and O1 do not. As noted above, compound (II) has a greater excess of potential acceptors than (I) and is thus expected also to have numerous significant C—H···O attractive interactions. Those C—H···O sets in the structure of (II) which satisfy the acceptance criteria listed above for (I) are nine in number and are listed in Table 4. These interactions involve six of the eight O atoms in the molecule including, in particular, the three O atoms not involved in O—H···O bonds.

In each of (I*A*), (I*B*) and (II), the three benzenoid rings are closely planar, the maximum deviation of any

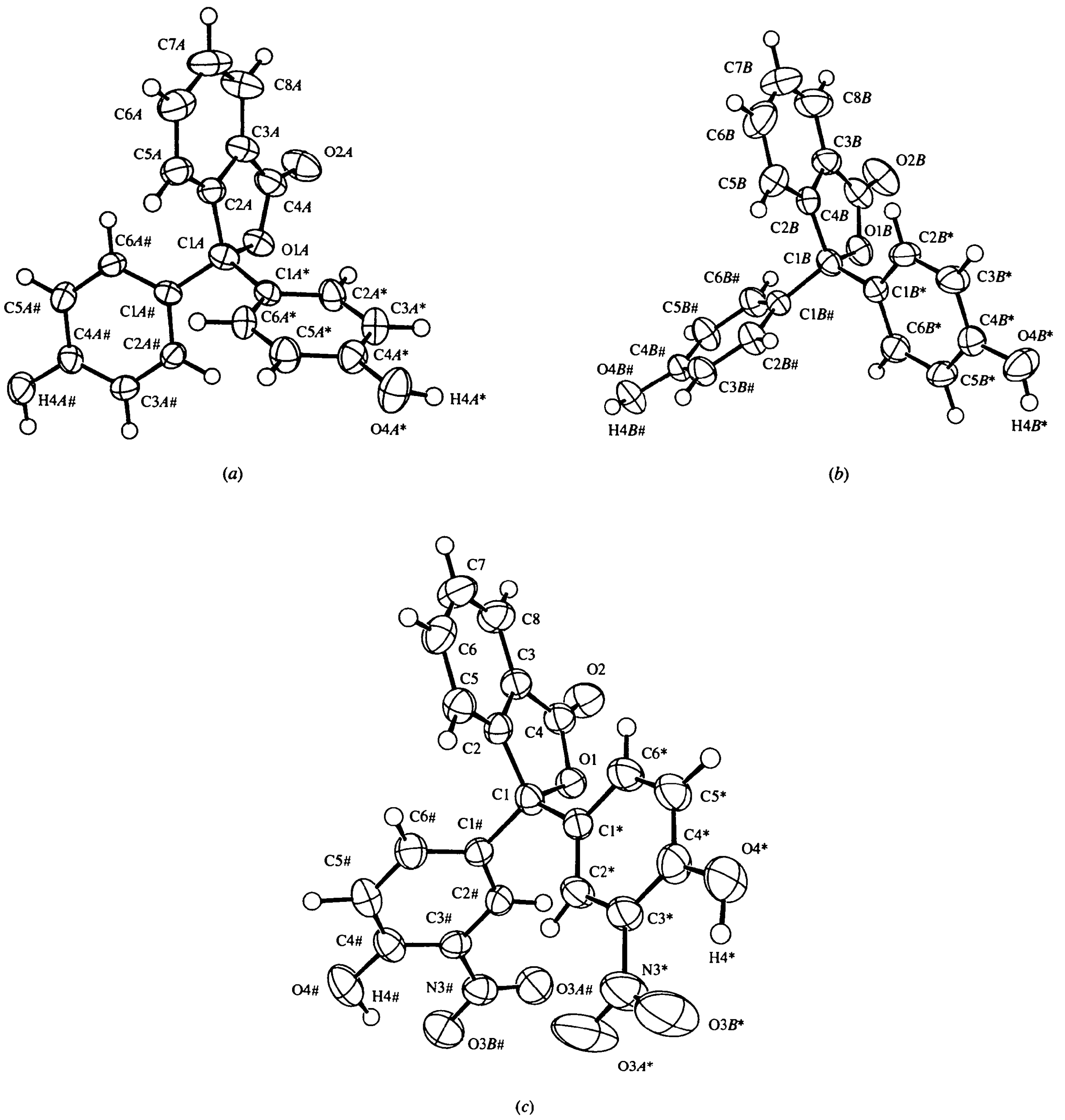


Fig. 1. *ORTEP*II (Johnson, 1976) drawings of (*a*) phenolphthalein molecule *A*, (*b*) phenolphthalein molecule *B* and (*c*) 3′,3″-dinitrophenolphthalein, showing our numbering schemes. Displacement ellipsoids are drawn at the 50% probability level for all non-H atoms. H atoms have been set artificially small.

involved atom from the appropriate best-fit plane being 0.013 (3) Å; the maximum deviation of an atom from the best-fit plane through the heterocyclic ring is 0.059 (5), 0.014 (4) and 0.044 (2) Å for (I*A*), (I*B*) and (II), respectively. The dihedral angles for these three sets of planes are given in Table 6. Further characterization of the molecular configurations is provided by the values of the torsion angles about the bonds between the substituted phenyl groups and the heterocyclic ring-C atom to which they are bonded. For (I*A*), these angles are: C2*A*—C1*A*—C1*A*#—C2*A*# −166.6 (3), C2*A*—C1*A*—C1*A**—C2*A** −96.3 (4) and C2*A*—C1*A*—C1*A**—C6*A** 79.2 (4)°; for (I*B*): C2*B*—C1*B*—C1*B*#—C2*B*# −90.7 (4), C2*B*—C1*B*—

C1B*—C2B* −11.0 (5) and C2B—C1B—C1B*—C6B* 174.4 (4)°, and for molecule (II): C2—C1—C1#—C2# 151.1 (2), C2—C1—C1*—C2* 133.6 (3) and C2—C1—C1*—C6* −44.5 (3)°. A point of interest is that the nitro groups of (II) are very nearly coplanar with the phenyl rings to which they are bonded.

Intramolecular distances and angles of special interest in (I) and (II) are given in Tables 1 and 3. All distances and angles appear to fall within normal ranges. Appropriate geometric comparisons for the heterocyclic portion of the phthalide group are provided by the phthalide form of 2-acetylbenzoic acid (Dobson & Gerkin, 1996). The maximum difference and the average difference for six distances (the five ring distances and the C4—O2 distance involving the heterocyclic portion of the phthalide group) between acetylbenzoic acid and (IA), (IB) and (II) are 0.012 and 0.008 (6) Å, 0.012 and 0.006 (6) Å, and 0.028 and 0.011 (5) Å, respectively. Thus, there is very good agreement among all these data with a single exception, the C4—O1 distance in (II), which differs by 0.025 Å from the mean of the other three values. The closest intermolecular approaches in (I), excluding pairs of atoms within directly hydrogen-bonded groups or C—H···O interaction sets, are between C5A# and H5A*^{vi} (symmetry code as in Table 2), and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.14 Å; similarly, the closest intermolecular approaches in (II) are between O3B* and C4^{ii} (symmetry code as in Table 4), and fall short of the corresponding Bondi sum by 0.08 Å.

Although extensive comparison of the structure of (II) with that of 3,3′,5,5′-tetrabromophenolsulfonphthalein (Veerapandian *et al.*, 1984), which also crystallized in a centrosymmetric space group, is precluded by the substantial differences in molecular constitution, its molecules also form dimers involving hydrogen bonds (between a phenol group as donor and the heterocyclic ring O atom as acceptor) in rings (of 16 atoms) disposed about centers of symmetry.

Experimental

Phenolphthalein was obtained as a white crystalline powder of reagent grade from the Reagent Laboratory of The Ohio State University. The solid was dissolved in methanol. Slow evaporation at room temperature yielded X-ray quality crystals. 3′,3″-Dinitrophenolphthalein was obtained as X-ray quality crystals from an attempted growth of an aromatic carboxylic acid from a solution containing nitric acid and phenolphthalein, which was used to monitor the acidity. One of these crystals was mounted for X-ray study under the assumption that it was the desired carboxylic acid, but analysis of the X-ray data established its identity as given here.

Compound (I)

Crystal data

$C_{20}H_{14}O_4$
$M_r = 318.33$
Orthorhombic
$Pna2_1$
$a = 19.270$ (4) Å
$b = 14.819$ (4) Å
$c = 11.392$ (4) Å
$V = 3253.2$ (13) Å^3
$Z = 8$
$D_x = 1.300$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.3$–$14.7°$
$\mu = 0.085$ mm^{-1}
$T = 296$ K
Uncut multifaceted chunk
0.46 × 0.38 × 0.35 mm
Colorless

Data collection

AFC-5S diffractometer
ω scans
Absorption correction: none
4192 measured reflections
4192 independent reflections
2250 reflections with $I > 2\sigma_I$
$\theta_{max} = 27.5°$

$h = 0 \rightarrow 25$
$k = 0 \rightarrow 19$
$l = -14 \rightarrow 0$
6 standard reflections every 150 reflections intensity variation: ±2.8% (average maximum relative intensity)

Refinement

Refinement on F^2
$R = 0.045$
$wR = 0.097$
$S = 1.04$
3923 reflections
449 parameters
H atoms: see below
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 3.5 (6) × 10^{-7}
Scattering factors from Stewart *et al.* (1965) (H) and Cromer & Waber (1974) (C, O)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1A—C1A	1.478 (4)	C1A—C1A#	1.521 (5)
O1A—C4A	1.346 (4)	C1A—C1A*	1.524 (5)
O1B—C1B	1.496 (4)	C1A—C2A	1.515 (5)
O1B—C4B	1.357 (5)	C1B—C1B#	1.525 (5)
O2A—C4A	1.222 (5)	C1B—C1B*	1.514 (5)
O2B—C4B	1.213 (5)	C1B—C2B	1.509 (5)
O4A#—C4A#	1.372 (5)	C2A—C3A	1.383 (5)
O4A*—C4A*	1.367 (5)	C2B—C3B	1.377 (6)
O4B#—C4B#	1.379 (4)	C3A—C4A	1.454 (6)
O4B*—C4B*	1.368 (5)	C3B—C4B	1.457 (6)
C1A—O1A—C4A	111.0 (3)	C2B—C3B—C4B	108.6 (4)
C1B—O1B—C4B	110.7 (3)	O1A—C4A—O2A	119.8 (4)
O1A—C1A—C2A	102.3 (3)	O1A—C4A—C3A	109.2 (4)
O1B—C1B—C2B	102.1 (3)	O2A—C4A—C3A	131.0 (4)
C1A—C2A—C3A	108.8 (3)	O1B—C4B—O2B	120.2 (4)
C1B—C2B—C3B	109.7 (3)	O1B—C4B—C3B	109.0 (4)
C2A—C3A—C4A	108.3 (3)	O2B—C4B—C3B	130.9 (5)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
O4A#—H4A#···O2A^{i}	0.92 (5)	1.72 (5)	2.631 (4)	176 (5)
O4A*—H4A*···O4A#^{ii}	0.87 (5)	1.85 (5)	2.712 (4)	174 (5)
O4B#—H4B#···O2B^{iii}	0.82 (4)	1.92 (4)	2.715 (4)	162 (4)
O4B*—H4B*···O4B#^{iv}	0.84 (5)	1.96 (5)	2.787 (4)	171 (5)
C2A*—H2A*···O2B^{v}	0.98	2.65	3.432 (5)	137
C3A*—H3A*···O4A#^{ii}	0.98	2.67	3.351 (5)	127
C5A—H5A···O4A*^{vi}	0.98	2.55	3.525 (5)	176
C6A*—H6A*···O4A*^{vi}	0.98	2.55	3.469 (5)	157
C6B#—H6B#···O1B	0.98	2.43	2.783 (5)	101

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, y, 1+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (v) $x, 1+y, 1+z$; (vi) $-x, 2-y, z-\frac{1}{2}$.

Compound (II)

Crystal data

$C_{20}H_{12}N_2O_8$
$M_r = 408.32$
Orthorhombic
Pbcn
$a = 27.634$ (2) Å
$b = 8.122$ (4) Å
$c = 15.741$ (3) Å
$V = 3533.1$ (16) Å^3
$Z = 8$
$D_x = 1.535$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.6$–$14.9°$
$\mu = 0.114$ mm^{-1}
$T = 296$ K
Cut column
$0.38 \times 0.27 \times 0.15$ mm
Yellow

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: none
4602 measured reflections
4602 independent reflections
1780 reflections with $I > 2\sigma_I$
$\theta_{max} = 27.50°$

$h = 0 \rightarrow 35$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 20$
6 standard reflections every 150 reflections intensity variation: ±2.0% (average maximum relative intensity)

Refinement

Refinement on F^2
$R = 0.050$
$wR = 0.122$
$S = 1.10$
4069 reflections
319 parameters
All H atoms refined
$w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Cromer & Waber (1974) (C, O, N)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C1	1.482 (3)	O4#—C4#	1.347 (3)
O1—C4	1.375 (3)	N3*—C3*	1.448 (3)
O2—C4	1.198 (3)	N3#—C3#	1.460 (4)
O3*A**—N3*	1.200 (3)	C1—C1*	1.523 (3)
O3*B**—N3*	1.226 (3)	C1—C1#	1.529 (3)
O3*A*#—N3#	1.207 (3)	C1—C2	1.518 (3)
O3*B*#—N3#	1.239 (3)	C2—C3	1.372 (3)
O4*—C4*	1.345 (3)	C3—C4	1.458 (4)
C1—O1—C4	110.8 (2)	O3*B*#—N3#—C3#	118.5 (3)
O3*A**—N3*—O3*B**	121.4 (3)	O1—C1—C2	102.1 (2)
O3*A**—N3*—C3*	120.2 (3)	C1—C2—C3	109.5 (2)
O3*B**—N3*—C3*	118.4 (3)	C2—C3—C4	109.0 (2)
O3*A*#—N3#—O3*B*#	122.4 (3)	O1—C4—O2	120.5 (3)
O3*A*#—N3#—C3#	119.0 (2)	O1—C4—C3	108.1 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4#—H4#···O3*B*#	1.06 (5)	1.67 (5)	2.572 (4)	141 (4)
O4#—H4#···O2^{i}	1.06 (5)	2.80 (4)	3.259 (3)	107 (3)
O4*—H4*···O3*B**	0.96 (4)	1.73 (5)	2.580 (3)	146 (4)
O4*—H4*···O2^{ii}	0.96 (4)	2.75 (4)	3.274 (3)	115 (3)
C2#—H2#···O1	0.94 (3)	2.52 (3)	2.771 (3)	96 (2)
C2#—H2#···O3*A*#	0.94 (3)	2.37 (3)	2.688 (4)	100 (2)
C2*—H2*···O3*A**	0.92 (2)	2.34 (2)	2.702 (4)	103 (2)
C5—H5···O4*^{iii}	0.98 (3)	2.67 (3)	3.527 (4)	147 (2)
C6—H6···O1^{iv}	0.95 (3)	2.66 (3)	3.593 (4)	167 (2)
C6—H6···O4#^{v}	0.95 (3)	2.72 (3)	3.084 (4)	104 (2)
C6#—H6#···O3*A*#^{iv}	0.94 (3)	2.50 (3)	3.319 (4)	146 (2)
C6*—H6*···O3*B**^{vi}	0.94 (3)	2.51 (2)	3.388 (4)	156 (2)
C8—H8···O3*A*#^{vii}	0.95 (3)	2.59 (3)	3.489 (4)	157 (2)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iv) $x, 1+y, z$; (v) $-x, 1-y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $x, -y, z-\frac{1}{2}$.

Table 5. *First- and basic second-level graph set descriptors involving hydrogen bonds designated (a)–(d) for (II) in the order given in Table 4*

	(*a*)	(*b*)	(*c*)	(*d*)
(*a*)	*S*(6)	$C_1^2(10)[S(6)]$	$D_2^2(17)$	–
(*b*)		$R_2^2(20)$	–	$C_2^2(20)$
(*c*)			*S*(6)	$C_1^2(10)[S(6)]$
(*d*)				*C*(10)

Table 6. *Dihedral angles (°) between various molecular planes in the title compounds*

Plane 1	Plane 2	(I*A*)	(I*B*)	(II)
C2–C8	#Phenyl	68.9 (2)	77.6 (2)	64.9 (1)
C2–C8	*Phenyl	76.1 (2)	74.2 (2)	77.3 (1)
C2–C8	C1–C4,O1	1.9 (2)	1.0 (2)	6.8 (1)
C1–C4,O1	#Phenyl	70.4 (2)	76.8 (2)	63.7 (1)
C1–C4,O1	*Phenyl	75.3 (2)	73.5 (2)	84.0 (1)
*Phenyl	#Phenyl	74.4 (2)	71.4 (2)	79.1 (1)
#NO_2	#Phenyl	–	–	3.7 (2)
*NO_2	*Phenyl	–	–	3.7 (3)

For both compounds, scan widths were (1.40 + 0.35 tanθ)° in ω, with a background/scan-time ratio of 0.5. The data were corrected for Lorentz and polarization effects. For (I), the Laue group assignment, systematic absences and intensity statistics consistent with acentricity indicated space group *Pna*2$_1$ (No. 33); since refinement proceeded well it was adopted. Fourier-difference methods were used to locate the initial H-atom positions. In the latter stages of refinement, all H atoms, except the four phenolic H atoms, were made canonical, with a C—H distance of 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom. The four phenolic H atoms were refined isotropically; the refined O—H distances appear in Table 2. The maximum effect of extinction was 6.2% of F_o for 02$\bar{2}$. The maximum positive residual peak was located 1.27 Å from C1*A**, and the maximum negative peak was located 1.11 Å from C1*B* and 1.17 Å from C2*B*. For (II), the Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group *Pbcn* (No. 60); since refinement proceeded well it was adopted. Fourier-difference methods were used to locate the initial H-atom positions. The H atoms were refined isotropically; the refined C—H distances ranged from 0.92 (3) to 1.12 (3) Å with a mean value of 0.96 Å (the O—H distances appear in Table 4). The predicted value of the extinction coefficient was negative so an extinction coefficient was not refined. The maximum positive residual peak was located ~0.8 Å from C8 and 0.9 Å from C7, and the maximum negative peak was located 0.13 Å from C2.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

We gratefully acknowledge support for LJF by PPG, Inc. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1369). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 3078–3081.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Veerapandian, B., Salunke, D. M. & Vijayan, M. (1984). *Acta Cryst.* C**40**, 500–502.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1998). C**54**, 539–540

8-Hydroxyquinolinium–Salicylate–Salicylic Acid (1/1/1) Complex, $C_9H_8NO^+.C_7H_5O_3^-.C_7H_6O_3$

JUSTIN ROBERT JEBAMONY AND PACKIANATHAN THOMAS MUTHIAH

Department of Chemistry, Bharathidasan University, Tiruchirapalli 620 024, Tamil Nadu, India. E-mail: sysop/trichi@dartmail.dartnet.com

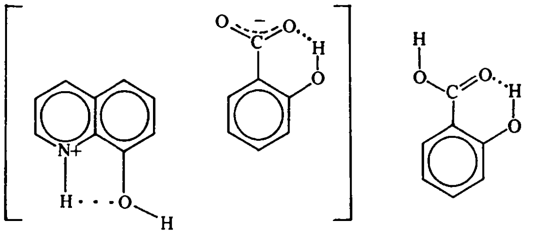
(*Received 1 July 1997; accepted 17 October 1997*)

Abstract

An intramolecular N1—H···O hydrogen bond is present in the 8-hydroxyquinolinium cation. An intramolecular hydrogen bond is present in each of the salicyl moieties (between the phenolic OH and the carboxy group). The crystal structure is stabilized by a network of intermolecular N—H···O, O—H···O and C—H···O hydrogen bonds.

Comment

Oxine (8-hydroxyquinoline) is a widely used analytical reagent. This moiety is also present in many anti-amoebic drugs. The present study has been undertaken as part of our research program on the hydrogen-bonding patterns and interactions in the crystal structures of oxines, their derivatives and their complexes in a variety of crystalline environments (Balasubramanian & Thomas Muthiah, 1996*a*,*b*). In the present study, a 1:2 complex, (I), of 8-hydroxyquinoline and salicylic acid, a widely used analgesic, has been prepared by mixing methanolic solutions of these two compounds in the molar ratio 1:2.



(I)

The asymmetric unit consists of one salicylic acid molecule, one salicylate anion and one 8-hydroxyquinolinium cation. 8-Hydroxyquinolinium is protonated at N1 leading to an enhancement of the internal angle at N1 compared with neutral quinoline moieties. The protonation also increases the difference between the external angles at C8 (Balasubramanian & Thomas Muthiah, 1996*b*). This is thought to have been caused by the intramolecular hydrogen bond, N1—H···O8. This intramolecular contact has also been observed in other 8-hydroxyquinoline structures (Banerjee *et al.*, 1984;

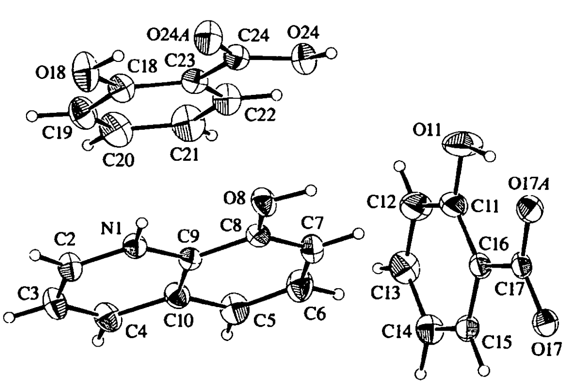


Fig. 1. An *ORTEP* (Johnson, 1965) view of the title compound with displacement ellipsoids at the 50% probability level.